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# **Sulphated Zirconia Catalysed Conversion of High density Polyethylene to value-added products using a Fixed-Bed Reactor**

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## **Abstract**

A sulphated zirconia catalyst (SZ) was investigated for catalytic conversion of high density polyethylene (HDPE) to liquid and gaseous hydrocarbons using a fixed-bed reactor. The SZ catalyst reduced the onset of degradation from 337°C for HDPE alone to 187°C with 10wt% SZ added. At 450°C a complete weight loss was obtained with the SZ addition against only 4wt% loss for HDPE only. Fixed-bed reactor experiments using 2g of HDPE with 10wt% SZ catalyst with a 30 minutes residence time showed a 98.0wt% conversion at temperature as low as 380°C. The liquid yield obtained was 39.0wt% with a composition of 16wt% paraffins, 21wt% olefins, 5wt% naphthenes and 58wt% aromatics. The carbon number distribution of the liquid was C<sub>7</sub>-C<sub>12</sub>, which is within the gasoline range. Equally, gaseous products ranging from methane up to different isomers of pentane which contained more paraffinic and naphthenic hydrocarbon were obtained. The sulphated zirconia catalyst was found to have high ammonia desorption (337.0 μmolNH<sub>3</sub>g<sup>-1</sup>), BET surface area (116.0 m<sup>2</sup>g<sup>-1</sup>), external surface area (112.0 m<sup>2</sup>g<sup>-1</sup>) and mesoporous structure. The overall results indicate that sulphated zirconia had excellent properties for catalytic conversion at temperature as low as 380°C with significant liquid yield which could offer a solution to plastic waste problem by converting the waste back into value-added chemicals and fuel.

**Key words:** plastic waste, HDPE, sulphated zirconia, fixed-bed reactor, TGA, catalytic conversion

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## Introduction

Catalytic conversion using heterogeneous catalyst has been identified as a potential option to convert plastic waste back into useable fuels and raw materials for the chemical industry [1-5]. A range of heterogeneous catalysts have been investigated, including zeolites (HZM-5, HUSY, HMOR), both fresh and spent FCC-based zeolites, MCM-41 and various silica-alumina systems and clay-based catalysts [3, 6-19]. A common feature of the catalysts used is conversion at temperatures above 450°C to generate primary gaseous species that can then enter the pore-space of the catalysts where the secondary reactions take place for producing the end products. Sulphated zirconia (SZ), or so-called super solid catalyst, has the potential to promote primary cracking of the polymer into oligomers at temperatures below 450°C and has thus been used as an excellent catalyst for oil refining processes, such as cracking and isomerisation [20-24]. Hence, SZ could be used during plastic waste conversion to promote conversion into short chain liquid and gaseous species at temperatures below 450 °C and may pave the way for a system to depolymerise ethylene-based polymers into liquids in the gasoline or diesel boiling point range.

The excellent activity of sulphated zirconia catalyst is traced to its super acidity composed of Brönsted and Lewis acid sites, large surface area, mesoporosity, thermal and chemical stability and simplicity in preparation [25]. The inductive effect of the S=O group from  $\text{SO}_4^{2-}$  in sulphated zirconia creates electronic deficiency that promote the Lewis acidity of Zr cation and thus promotes its acidity to super acidity. Sulphated zirconia has been reported to possess exceptional catalytic properties that could promote effective conversions of hydrocarbons to highly branched alkanes with high octane number at low temperature, where its catalytic structure and activity can be tailored by calcination [24]. It has been studied for many years and reported to be a very effective catalyst used in catalysing many processes in the oil refining and petrochemical industries [41, 42]. Apart from alkane isomerisation, sulphated zirconia was

also reported to be very efficient catalyst in many important processes, namely, hydrocracking, alkylation, condensation, esterification, acylation, oligomerisation and many organic synthesis reactions [21, 22, 26-31]. Sulphated zirconia with the aforementioned properties may offer an excellent catalytic activity in converting plastic, which is naturally viscous and has bulky structure. The use of sulphated zirconia for plastic conversion has not been reported to the best of best of the authors' knowledge and could pave way for low temperature and tailored conversion of plastic waste into valuable liquid streams.

This work is aimed at evaluating sulphated zirconia catalyst for the conversion of high density polyethylene (HDPE) into value-added hydrocarbon products. This study also examines effect of temperature on product yields and in particular liquid product which could be used as fuel or industrial raw materials. The main focus is to find the applicability of sulphated zirconia in converting plastic waste to hydrocarbon products with gasoline range compositions at low temperature. Hence, developing a possible method for plastic waste recycling that is sustainable and cost-effective using sulphated zirconia catalyst.

## **2. Experimental**

### **2.1 Materials**

High density polyethylene 3mm pellets (HDPE, Sigma-Aldrich, UK) with a density of 0.952 g/mL, melt index of 42g/10min with 99.9% purity were grounded to 0.05 - 0.25mm using an SM2000 Retch Milling Machine. Table 1 lists the proximate and elemental compositions of the HDPE using a Thermo Scientific Flash Elemental Analyser (Flash EA, 1112 series). A 7Mol%  $\text{SO}_3$  solid acid sulphated zirconia catalyst with a 100-150 $\mu\text{m}$  particle size range was supplied by MEL chemicals, UK. The catalyst was calcined in air for four hours at 550°C using a Muffle furnace, cooled and kept in desiccators prior to use.

Table 1. Physicochemical Composition of the HDPE sample Used in this work

Sample	Proximate analysis(dry) wt%			Elemental composition (%)				
	Volatile matter	Ash	Fixed carbon	C	H	N	O	S
<b>HDPE</b>	96.83	0.00	3.17	85.7	14.1	0.00	0.00	0.00

## 2.2 Catalyst characterisations

Surface morphology and elemental/oxide composition of the catalyst were analysed using a FEI QUANTA 600F scanning electron microscopy (SEM) version 2.4 coupled with a Genesis spectrum version 5.21 EDX analyser. Powder X-ray diffraction (XRD) patterns were obtained using a Hiltonbrooks DG 3 operated at 40kv with a 20mA Philips PW 1050 goniometer, proportional detector and monochromatic Cu K $\beta$  radiation. The scanning was carried out at a scan speed of 2° (2 $\theta$ ) min<sup>-1</sup> across a range 5-65° with a step size of 0.05°. A Micrometrics Gemini VII 2390 V3.03 surface area/porosity analyser was used to measure the BET surface area of the catalyst under nitrogen adsorption. The ammonia temperature programmed desorption (TPD) was carried out using a Quantachrome ChemBET TPR/TPD instrument, which was fitted with a TPRWin version 3.5 software for data analysis. Approximately 0.5g of the catalyst sample was degassed for 30 minutes at 250°C under helium, cooled to 50°C and exposed to 30 ml min<sup>-1</sup> ammonia gas for ten minutes. Weakly physisorbed ammonia was purged with helium for 30 minutes before the TPD analysis from 50°C to 700°C with a heating rate of 10°C min<sup>-1</sup>.

## 2.3 Analysis

The TGA analysis was conducted in duplicates under nitrogen using a Perkin-Elmer Pyris1 thermogravimetric analyser (TGA1) at 10°C/min from 35 to 900°C on 20 mg. The liquid products obtained from the fixed-bed reactor outlined in Section 2.4 were diluted with 9 parts

DCM and analysed using a Variant CP-3800 Gas Chromatograph interfaced to a 1200 Quadrupole mass spectrometer with an ionising energy of 70 eV, source temperature of 280°C and a VF-1MS fused silica capillary column (50 m x 0.32 mm i.d.) coated with BPX5 (0.25 µm film thickness). Helium was employed as the carrier gas and a programme temperature was set at 50°C for 2 min, then increased to 300°C at a heating rate of 5°C min.<sup>-1</sup> and remained there for 30 min. The gaseous products from the fixed-bed reactor outlined in Section 2.4 were analysed using a Perkin Elmer Clarus 580 Gas Chromatograph (GC) fitted with both a Flame Ionization Detector (FID) and a thermal conductivity detector (TCD) both operating at 200°C. About 5 µl of the gas sample was injected with helium as the carrier gas and held at 60°C and remained for 13 minutes then increased by 10°C min<sup>-1</sup> to 160°C and remained there for another 13 minutes.

## **2.4 Procedure**

Figure 1 shows the schematic diagram of the fixed-bed reactor system used for the catalytic conversion of HDPE. A 1.0 inch horizontal stainless steel tube holding a stationary alumina crucible containing the sample was heated using a Carbolite furnace with programmable temperature controller. A 30 min nitrogen purge at 30cl/min was used prior to heating the reactor at 20°C min<sup>-1</sup> to 380°C using 30 minutes residence time for the conversion. The HDPE conversion was repeated at temperatures from 380 to 430°C keeping all other parameters constant. The condensable liquid product was collected through a cooling trap made up of three conical flasks immersed in an ice bath while the volatile product was purged from the reactor by the 30cl min<sup>-1</sup> nitrogen for sampling. The condensable liquid product was collected by rinsing all the conical flasks and connecting tubes with DCM. The dissolved liquid was dried and transferred into glass bottles and stored in a fridge for next analysis. The gaseous product

was passed through the exhaust trap and sample gas was collected using gas bags and immediately analysed using the GC/FID/TCD. The weight percentages of the product yields were calculated as the mass of a particular product obtained divided by the initial mass of HDPE multiply with 100 [10, 32, 33]. The coke residue was calculated by subtracting the catalyst weight from the residue and dividing this by the original HDPE weight.

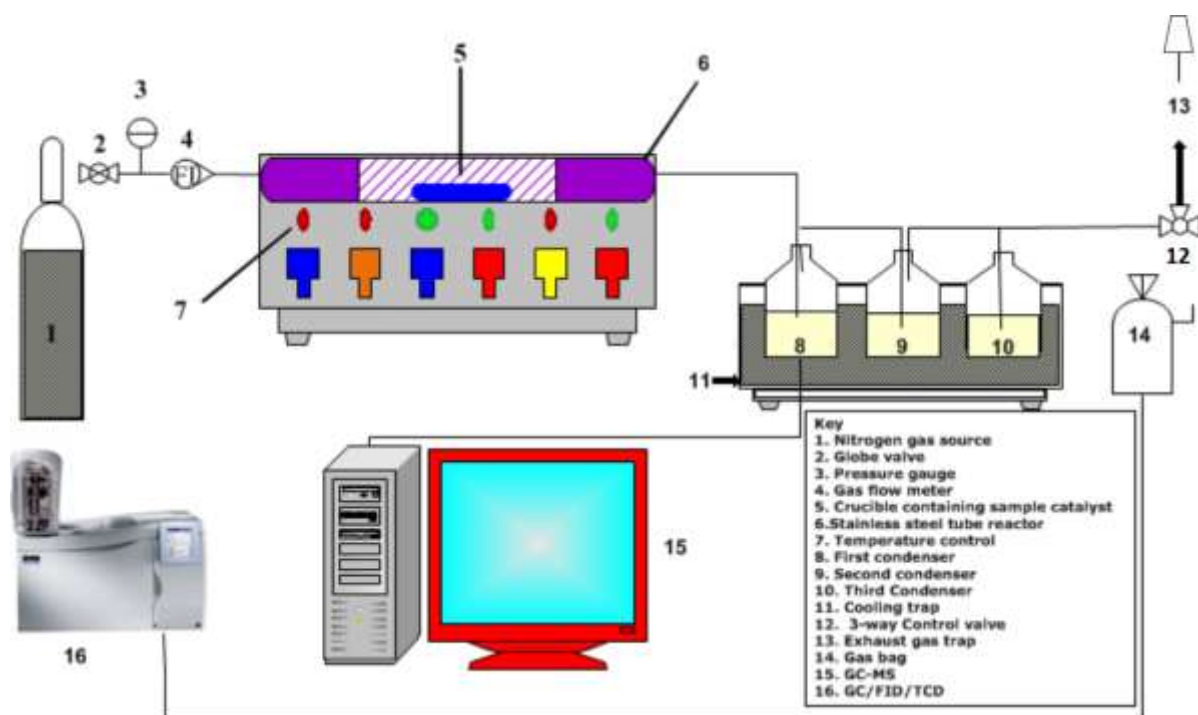


Figure 1 Schematic diagram of a fixed bed reactor set-up for the for HDPE catalytic conversion.

### 3. Results and discussion

#### 3.1 Catalyst Characterisation

Table 2 summarises the physicochemical characteristics of sulphated zirconia (SZ) catalyst. It has a BET surface area of  $116 \text{ m}^2 \text{ g}^{-1}$  and external surface area of  $112 \text{ m}^2 \text{ g}^{-1}$  with a micropore volume and micropore area of  $0.0011 \text{ cm}^3 \text{ g}^{-1}$  and  $0.21 \text{ m}^2 \text{ g}^{-1}$ , respectively. This shows that the total surface area of the catalyst is virtually external. The BET surface area of the SZ is also comparable to what has been reported in the literature [35][36]. The  $\text{N}_2$ -adsorption isotherm in Figure 2 shows that the SZ catalyst had a high nitrogen adsorption of about  $1.10 \text{ mmol/g}$  at low relative pressure ( $P/P^0 < 0.1$ ) associated with micropores [9, 34]. The  $\text{N}_2$ -adsorbtion

isotherms also shows a slight capillary condensation over the relative pressure range of 0.4 to 0.9 which is a typical feature of mesoporous material [5, 9, 36-40]. The increasing adsorptions at higher relative pressure ( $p/p^0$ ) above 0.9 may indicate the presence of some macroporous material. But overall, the sulphated zirconia can be regarded as mainly mesoporous with some micro and macro pores. The SEM microgram in Figure 3 indicates that the catalyst had a non-uniform particle sizes ranging from 100 to 200nm. However, there are some visible open voids in between the particles. The catalyst had an  $\text{SO}_3$  content of 6.64 Mol % as measured by the SEM environmental analysis in Figure 3, which supports the high acidity of  $337.0 \mu\text{molNH}_3\text{g}^{-1}$  observed from the ammonia TPD, which was believed to be responsible for the catalyst acidity [37-39].

The powder X-ray (XRD) diffraction pattern of the SZ after the calcination at  $550^\circ$  in Figure 4 shows that the crystal phase of the SZ contained exclusively tetragonal  $\text{ZrO}_2$  (JCPD no. 50-1089), where the four peaks in the diffractograms were observed at  $2\theta = 30.41$  (relative intensity is 100) as well as at 35.25 (20), 50.71(52) and 60.28 (31). This is similar to what was previously reported in literature [30, 36, 41-45]

Table 2 Characteristics of sulphated zirconia catalyst used for HDPE conversion

Characteristics	Sulphated zirconia
BET surface area ( $\text{m}^2 \text{g}^{-1}$ )	116
External surface area ( $\text{m}^2 \text{g}^{-1}$ ) <sup>a</sup>	112
pore volume ( $\text{cm}^3 \text{g}^{-1}$ ) <sup>b</sup>	0.21
Average pore size (nm) <sup>b</sup>	10.8
Micropore volume ( $\text{cm}^3 \text{g}^{-1}$ ) <sup>a</sup>	0.0011
Micropore area ( $\text{m}^2 \text{g}^{-1}$ ) <sup>a</sup>	4.22
Ammonia desorption ( $\mu\text{mol NH}_3 \text{g}^{-1}$ ) <sup>c</sup>	142.0, 158.5 & 37.1
Tmax ( $^\circ\text{C}$ )	229, 365 & 630
$\text{SO}_3$ (Mol %) <sup>d</sup>	6.64

<sup>a</sup>t-plot

<sup>b</sup> H-K method at  $p/p^0 = 0.95$

<sup>c</sup>  $\text{NH}_3$  TPD, three desorption peaks; two in weak and medium acid site temperature region while one at strong acid site region



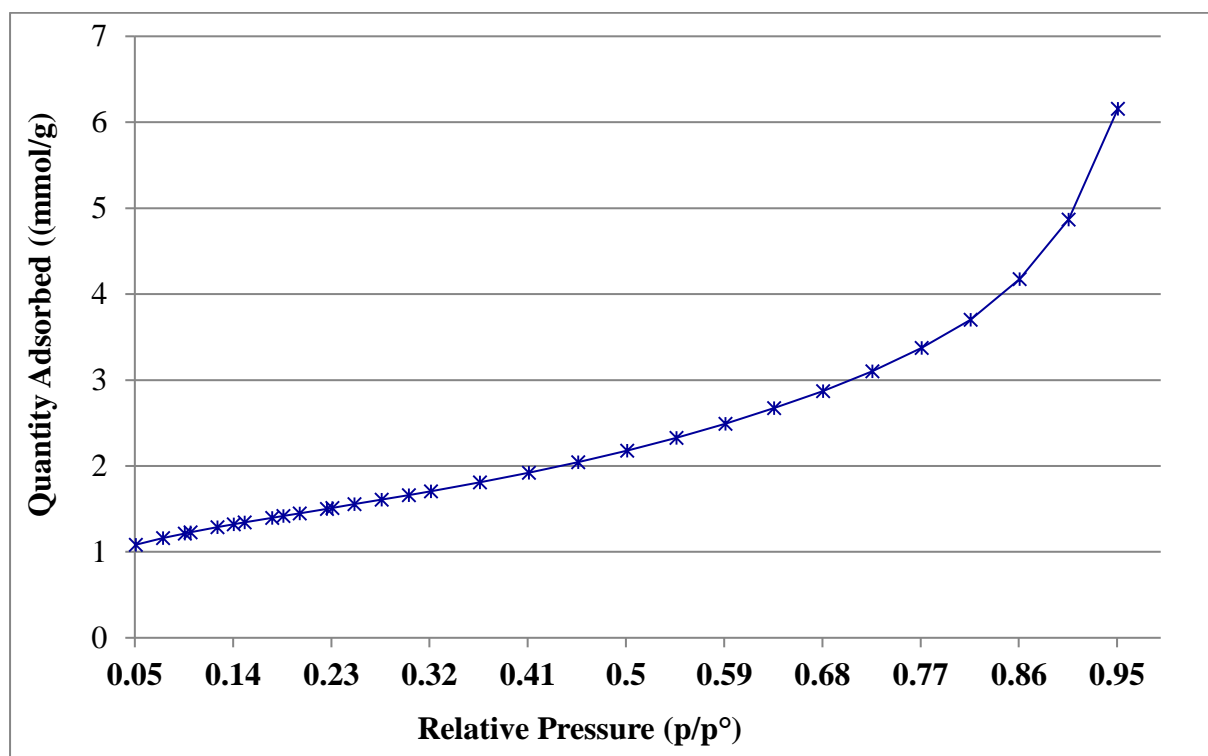


Figure 2 N<sub>2</sub>-adsorption isotherm of the calcined sulphated zirconia catalyst.

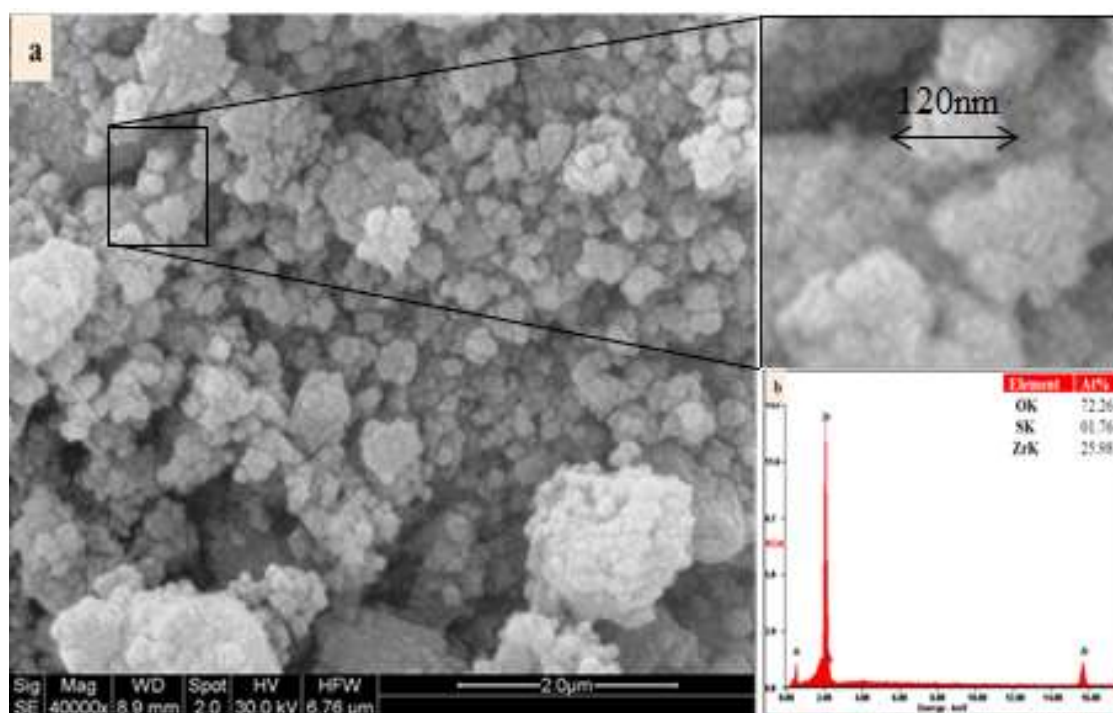


Figure 3 SEM microgram showing the surface morphology and elemental composition of the sulphated zirconia catalyst calcined at 550°C.

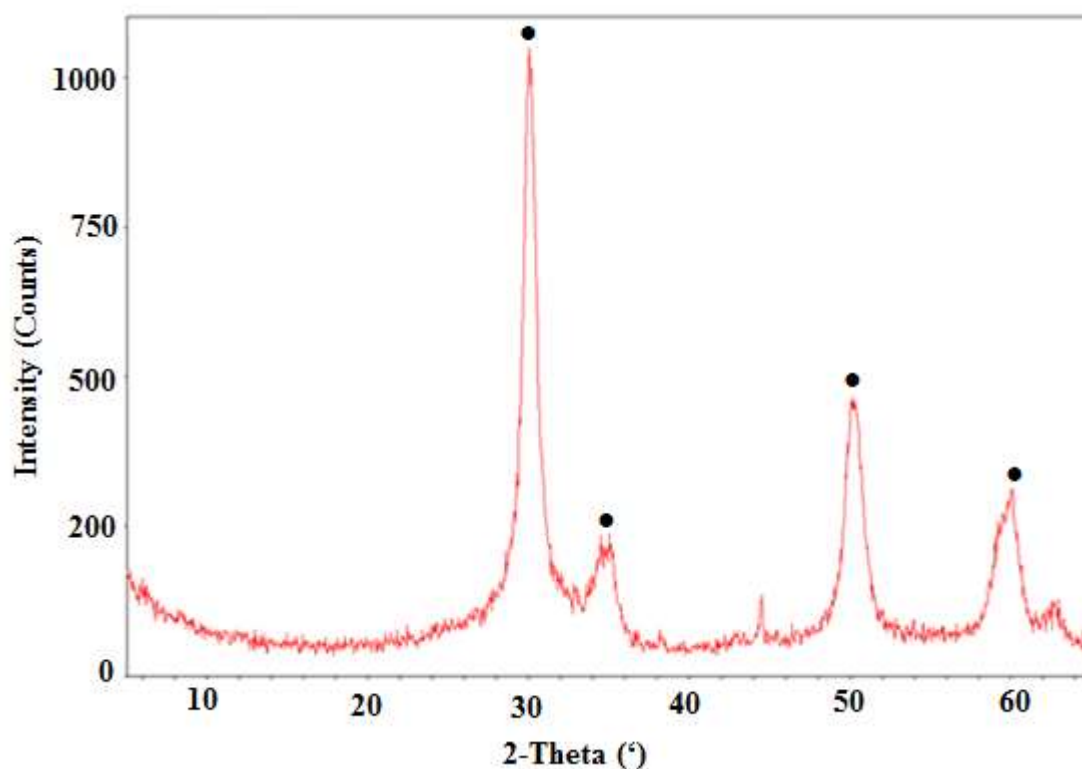


Figure 4 Powder XRD diffraction pattern of the sulphated zirconia catalyst.

### 3.2 Thermal analysis (TGA) and catalyst testing

The thermal gravimetric analysis (TGA) and the differential thermal gravimetric analysis (DTG) in Figure 5 comparing HDPE only with that of HDPE mixed with 10wt% sulphated zirconia catalyst shows that the onset weight loss of HDPE only commenced at 337°C while in the presence of 10wt% SZ the temperature was significantly reduced to 187°C. At 450°C, only about 4wt% weight loss was achieved for HDPE only whereas nearly 94wt% weight loss was achieved using 10wt% SZ. The DTG temperature of maximum degradation rate ( $\Delta T_{\max}$ ) was reduced from 494°C for HDPE only to 419°C in the presence 10wt% SZ indicating that SZ

could offer an excellent activity towards HDPE conversion at low temperature. The excellent activities shown by the SZ catalyst may derive from its high acidic strength of 337.0  $\mu\text{molNH}_3\text{g}^{-1}$ ), and large BET external surface area of 112  $\text{m}^2 \text{g}^{-1}$  which are requisite factors needed to initiate the cracking of macromolecule at a low temperature. According to Aguado *et al.*, [46], the presence of external acid site contribute largely for the observed high cracking activity of the catalyst even at lower temperature. The large number of acid sites on the surface of a catalyst ease the cracking of bulky polymeric chain and may yield hydrocarbon compounds in the liquid range. Based on the DTG result, which shows rapid degradation commencing at 370°C and 419°C as temperature of maximum conversion rate ( $\Delta T_{\text{max}}$ ) in the presence of the SZ catalyst, a temperature range between 370 °C and 430°C was used for the fixed-bed reactor tests in order to find the temperature that gives the maximum conversion and highest liquid yield.

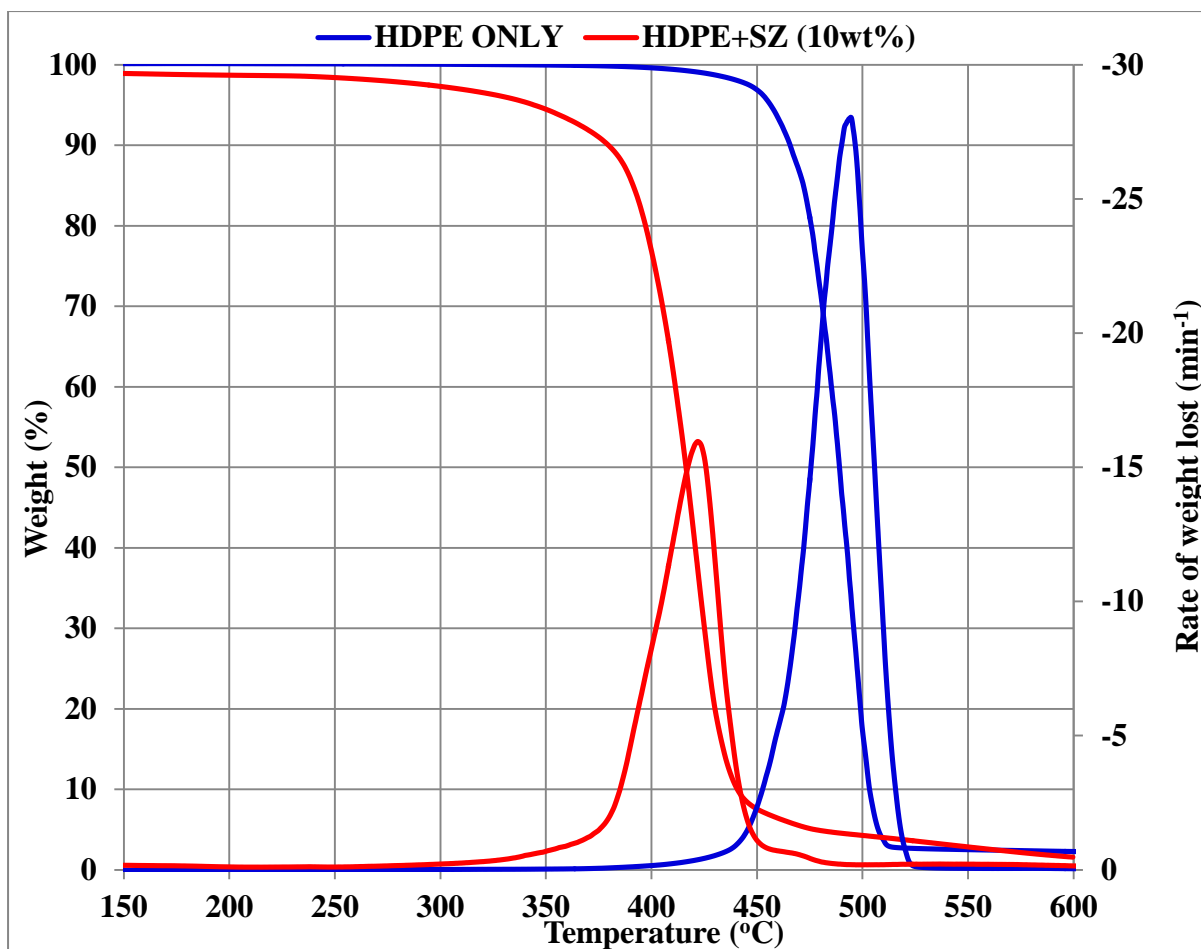
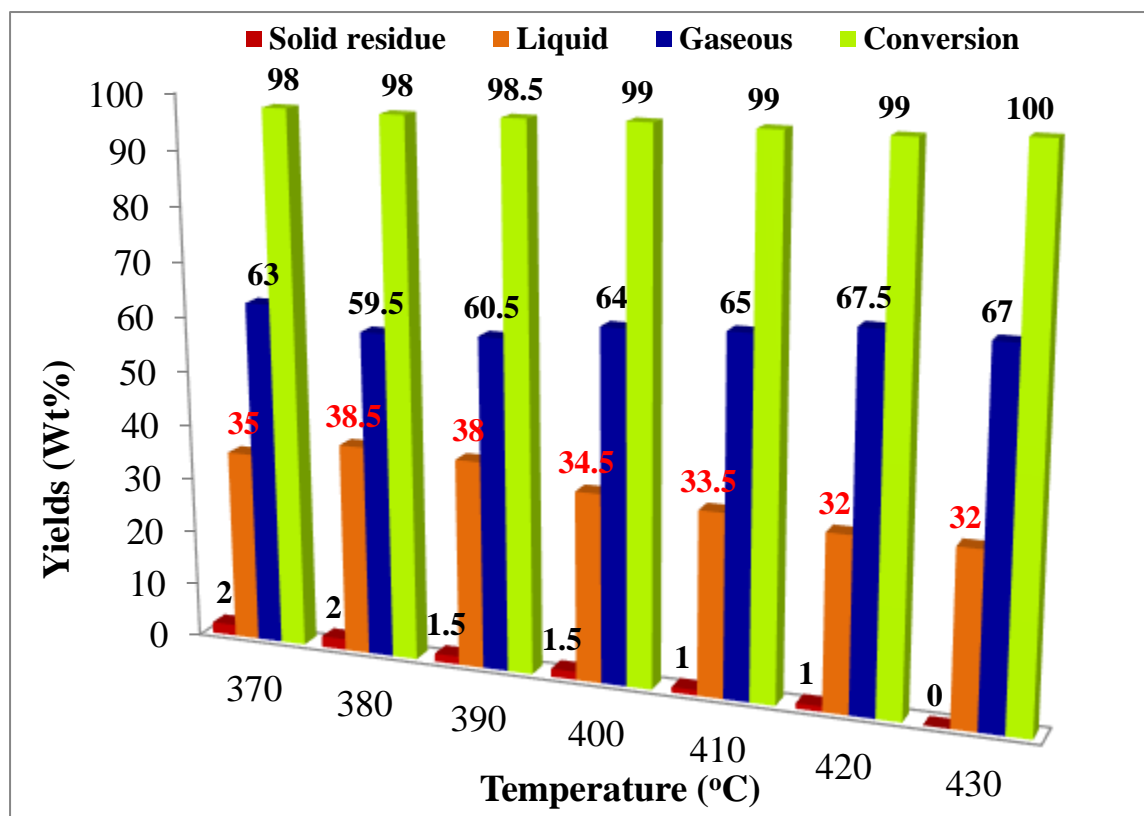


Figure 5 TGA and DTG curves comparing the conversion of HDPE only with catalytic degradation in the presence of 10wt% sulphated zirconia.

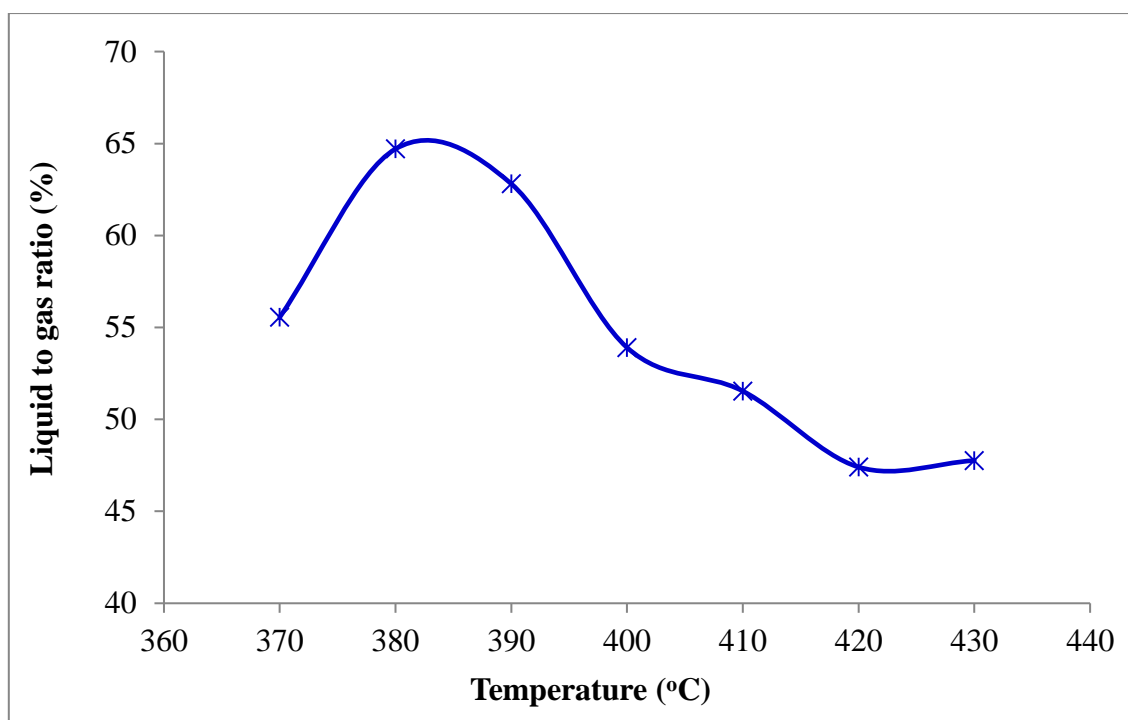
### 3.3 HDPE fixed-bed Catalytic conversion

The fixed-bed HDPE conversions and products yield obtained in the presence of the SZ catalyst at different conversion temperatures ranging from 370 to 430°C in Figure 6 shows that the HDPE conversion increased from 98.0wt% at 370°C to virtually 100wt% at 430°C. The liquid yield peaked at 380°C with 38.5 wt% and then decreased continuously to 32.0wt% at 430°C. The gaseous product followed an opposite trend by reaching a minimum of 59.5wt% at 380°C and then increased to 68 wt% at 430°C. The unconverted residue decreased from 2.0wt% at 370°C to virtually zero at 430°C. So, 380 and 390°C appeared as temperatures with optimal liquid yields. This is supported by Figure 7, which shows that 380°C gives the optimal liquid

to gas ratio. The results indicate that in the presence of an acidic catalyst, such as  $337.0 \mu\text{molNH}_3\text{g}^{-1}$  of the SZ catalyst, high temperature promotes excessive cracking and secondary reactions resulting in an increase in the gaseous yield and decrease in liquid yield which is also has been reported else ([10, 12, 47]. However, both literature and this study have shown that although the change in temperature from  $380^\circ\text{C}$  to  $430^\circ\text{C}$  does appear to have an influence on the quantities of liquid and gaseous products, the overall liquid composition does not significantly change. In view of this, only the liquid and gaseous products obtained at the optimal temperature of  $380^\circ\text{C}$  were analysed for detailed hydrocarbon composition as given in Sections 3.4 and 3.5.



**Figure 6** Comparison of conversions and products yield achieved from catalytic conversion of HDPE at 370 to  $430^\circ\text{C}$  in a fixed-bed reactor.



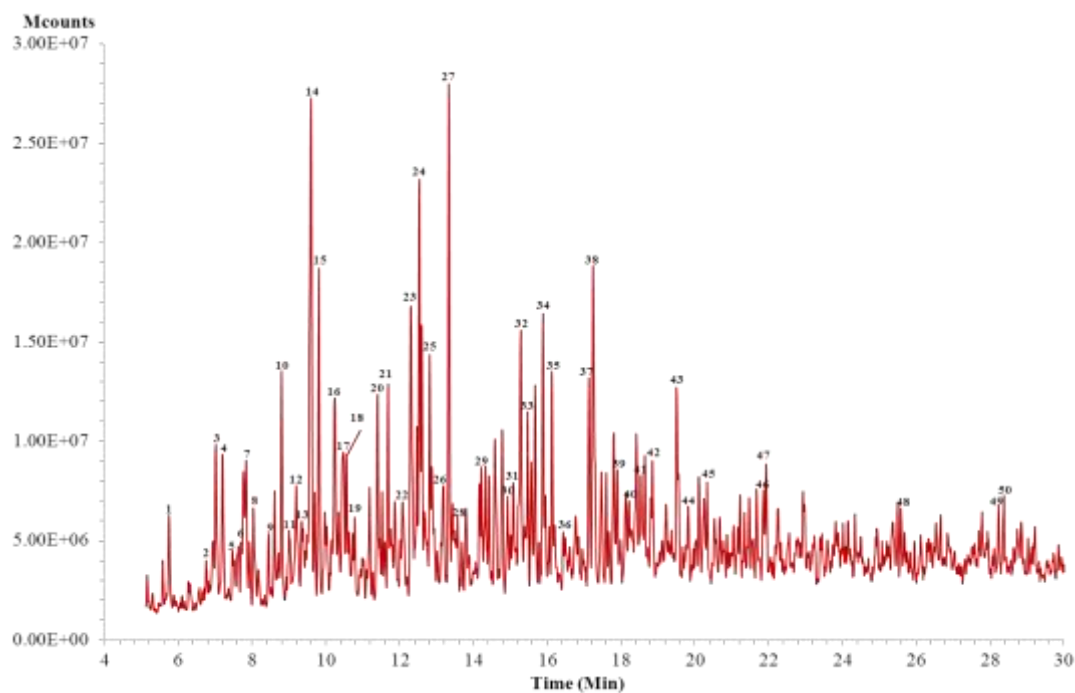
**Figure 7** Comparison of liquid to gas (L/G) ratio from catalytic conversion of HDPE at 370 to 430°C.

### 3.4 Liquid product analysis

A total of 50 peaks were identified in Figure 8 from the GC/MS chromatogram of the liquid product obtained at 380°C, where the optimal liquid yield was obtained in the presence of the SZ catalyst, and their retention times, peak areas and compound names are given in Table 3. Figure 8 compares the carbon atom distribution of the hydrocarbon compounds identified in the liquid product, where C9 accounts for more than 30% of all the compounds while C7 and C13 showed the least compositions. The order dominance of the hydrocarbon compounds in the liquid is in the following sequence, C7 < C13 < C12 < C8 < C11 < C10 < C9. This shows that the catalyst had promoted the hydrocarbon compounds in the gasoline and diesel boiling point range with very insignificant amount of C13 and larger compounds [29, 32, 48-51]. This make the liquid hydrocarbon obtained in the presence of sulphated zirconia catalyst a potential feedstock for transport fuel [32]. This feature of promoting hydrocarbons between C8 to C12

could be linked to the acidic and textural properties of the catalysts that promote end-chain cracking of the HDPE chain and produce hydrocarbon compounds useful for fuels [18, 47].

Figure 9 compares the relative amount of hydrocarbon compounds, namely paraffins, olefins, naphthens and aromatics (PONA) in the liquid product. The liquid obtained in the presence of sulphated zirconia catalyst appears to contain all the four hydrocarbon compounds in different proportion of 16wt% paraffins, 22wt% olefins, 5wt% naphthens and 58wt% aromatic. The SZ catalyst showed high selectivity towards aromatic compounds than the rest of the hydrocarbons similar to that reported for HZSM-5 (75.6wt % aromatics), HNZ (50.7wt%) and Ga-ZSM-5 (>80wt%) [49, 52]. Normally, highly acidic catalysts with large surface area mainly result in high gas yield while the SZ catalyst appears to promo liquids at low temperatures [5, 18]. The formation of aromatics could be related to carbenium ion formed during cracking of the HDPE chain that promotes dehydrocyclisation and produces aromatic compounds and saturated gaseous species. The selectivity of a catalyst towards a particular hydrocarbon compound is subject of intense debate but it is generally linked with its properties, which include surface morphology, surface area and acidic strength, as well as other factors, such as reactor type, reaction conditions and polymer type [46]. Hence, catalysts such as SZ with high surface area may offer less diffusional hindrance and easy accessibility to the acid sites located on the surface.



**Figure 8** The GC/MS chromatograms of the liquid product obtained at the temperature of 380°C where an optimum liquid yield was obtained during thermal conversion of HDPE using sulphated zirconia catalyst. Fifty peaks were identified and labelled 1-50.

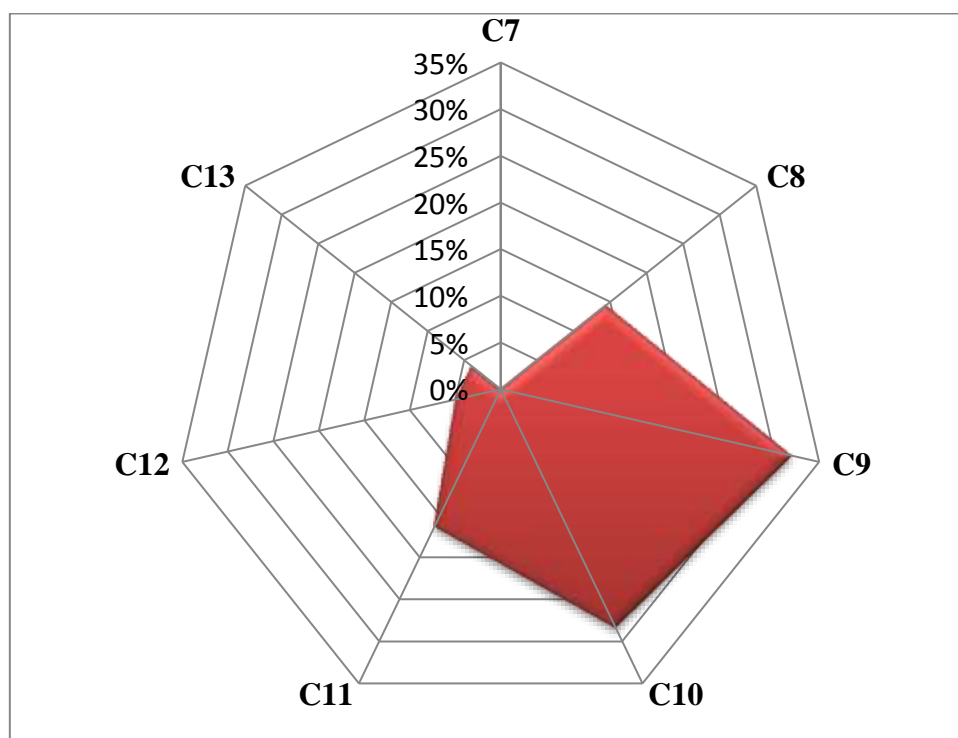




Figure 8 Comparison of the carbon number distributions of the hydrocarbon compounds in the liquid product obtained at 380°C using the sulphated zirconia catalyst.

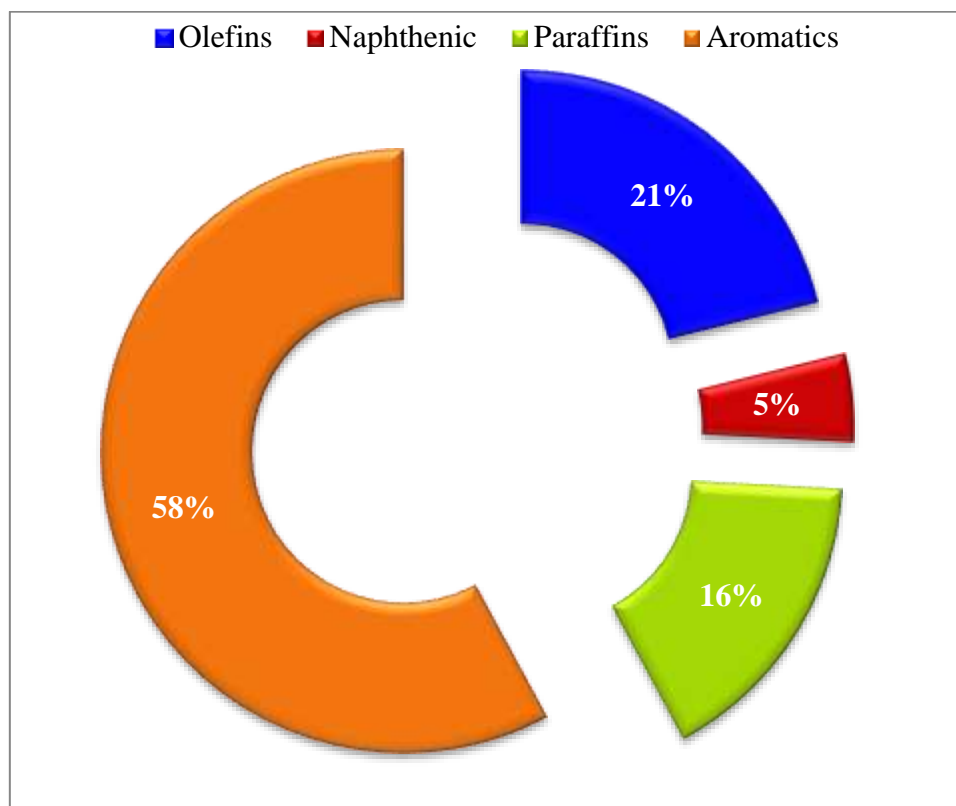


Figure 9 Comparison of the relative amount of paraffins, olefins, naphthens and aromatic compounds (PONA) in the liquid product obtained at 380°C.

Table 3 Summary of the detailed hydrocarbon composition of the liquid product obtained at 380°C where the optimal liquid yield was obtained in the presence of sulphated zirconia catalyst.

Peak level	Residence Time	Relative Amount (%)	Structural formula	Molecular formula
1	5.732	0.001	3-Heptene	C7H14
2	6.773	0.758	3-Ethyl-2-methylpent-2-ene	C8H16
3	7.001	2.049	2-Methylheptane	C8H18
4	7.18	1.514	2-Methylheptane	C8H18
5	7.468	0.991	6-methylhept-2-ene	C8H16
6	7.611	0.965	3-Ethylhex-2-ene	C8H16
7	7.839	1.958	2-Methylhept-2-ene	C8H16

8	8.041	1.394	3,5-Dimethylhex-2-ene	C8H16
9	8.445	1.104	3-Ethylhexane	C8H18
10	8.779	2.940	3,5-Dimethylheptane	C9H20
11	9.001	1.198	4-Ethylhept-3-ene	C9H18
12	9.193	1.692	4-Ethylhept-3-ene	C9H18
13	9.348	1.298	1,2,3-trimethylcyclohexane	C9H18
14	9.563	3.702	p-xylene	C8H10
15	9.836	1.468	3-Ethylheptane	C9H20
16	10.264	1.858	cis-4-Nonene	C9H18
17	10.447	2.001	4-Ethylhept-3-ene	C9H18
18	10.545	1.555	2-Methyloct-2-ene	C9H18
19	10.779	1.339	3-Nonene	C9H18
20	11.417	1.792	4-Methylnonane	C10H22
21	11.724	1.006	5-Decene	C10H20
22	12.094	1.379	2,6-Dimethyloct-2-ene	C10H20
23	12.309	3.659	1-Ethyl-3-methylbenzene	C9H12
24	12.537	5.053	1,2,4-Trimethyl benzene	C9H12
25	12.802	2.439	3-Ethyl-octane	C10H20
26	13.173	1.662	4-Decene	C10H20
27	13.328	6.076	1,3,5-trimethylbenzene	C9H12
28	13.568	1.365	2-Methylnon-2-ene	C10H20
29	14.217	1.893	1,3,5-trimethylbenzene	C9H12
30	14.953	1.069	1,1-Dimethyl-2-propyl cyclohexane	C11H22
31	15.096	1.448	1-Methyl-4-propylbenzene	C10H14
32	15.288	3.376	1-ethyl-2,4-dimethyl benzene	C10H14
33	15.421	1.154	2,2,6-trimethylcyclohexane	C11H22
34	15.897	2.788	1-ethyl-2,4-dimethyl benzene	C10H14
35	16.125	2.940	1-Pentyl-2- propylcyclopropane	C11H22
36	16.435	1.183	1,2,3,4- Tetramethylbenzene	C10H14
37	17.142	2.592	1,2,3,4- Tetramethylbenzene	C10H14
38	17.238	4.073	1-Methyl-4-(1- methylpropyl) benzene	C11H16
39	17.902	1.860	1,2,4,5,- tetramethylbenzene	C10H14
40	18.224	1.520	2,3-Dimethyldecane	C12H26
41	18.525	1.799	1-Methyl-4-(1- methylpropyl) benzene	C11H16
42	18.819	1.359	1-Ethyl-2,4,5- trimethylbenzene	C11H16
43	19.503	2.766		

44	19.817	5.009	1-Ethyl-2,4,5-trimethylbenzene	C11H16
45	20.356	1.167	2,3-Dimethylundecane	C13H28
46	21.864	1.644	1,3,5-trimethyl-2-propylbenzene	C12H18
47	21.934	1.930	Pentamethylbenzene	C11H16
48	25.586	1.442	1,4-Dimethylnaphthalene	C12H12
49	28.238	1.472	2,3,6-Trimethylnaphthalene	C13H14
50	28.359	1.302	1,6,7-Trimethylnaphthalene	C13H14

### 3.5 Gaseous product analysis

The GC/FID chromatogram of the gaseous products obtained at 380°C in Figure 10 shows different C1-C5 gaseous hydrocarbon compounds labelled 1 to 17. Table 4 summarises the detailed composition of all the peaks identified and their relative compositions in percentages.

The gaseous product obtained using sulphated zirconia catalyst contain broad mixture of hydrocarbon components ranging from methane to different isomers of pentane. This shows that the gaseous product obtained contained more paraffinic and naphthenic hydrocarbon compounds than olefinic. This is in line with the composition of the liquid obtained using sulphated zirconia catalyst where large proportion of aromatic hydrocarbon was obtained. It is expected that after dehydrocyclisation of the carbenium ion to form aromatics there is surplus of hydrogen that is used to form more saturated hydrocarbon compounds in the gas phase.

Figure 11 compares the carbon number distribution of the gaseous product obtained at 380°C where an optimal liquid yield was obtained using sulphated zirconia catalyst. The composition of the gaseous product showed that the relative amount of hydrocarbon compounds increases with increasing carbon atom number where C1 and C2 compounds are the least and C5 the most predominant. The order of predominance is in the following sequence, C1 < C2 < C3 < C4 < C5. The C6 hydrocarbon were outside the detection range of the GC/FID.

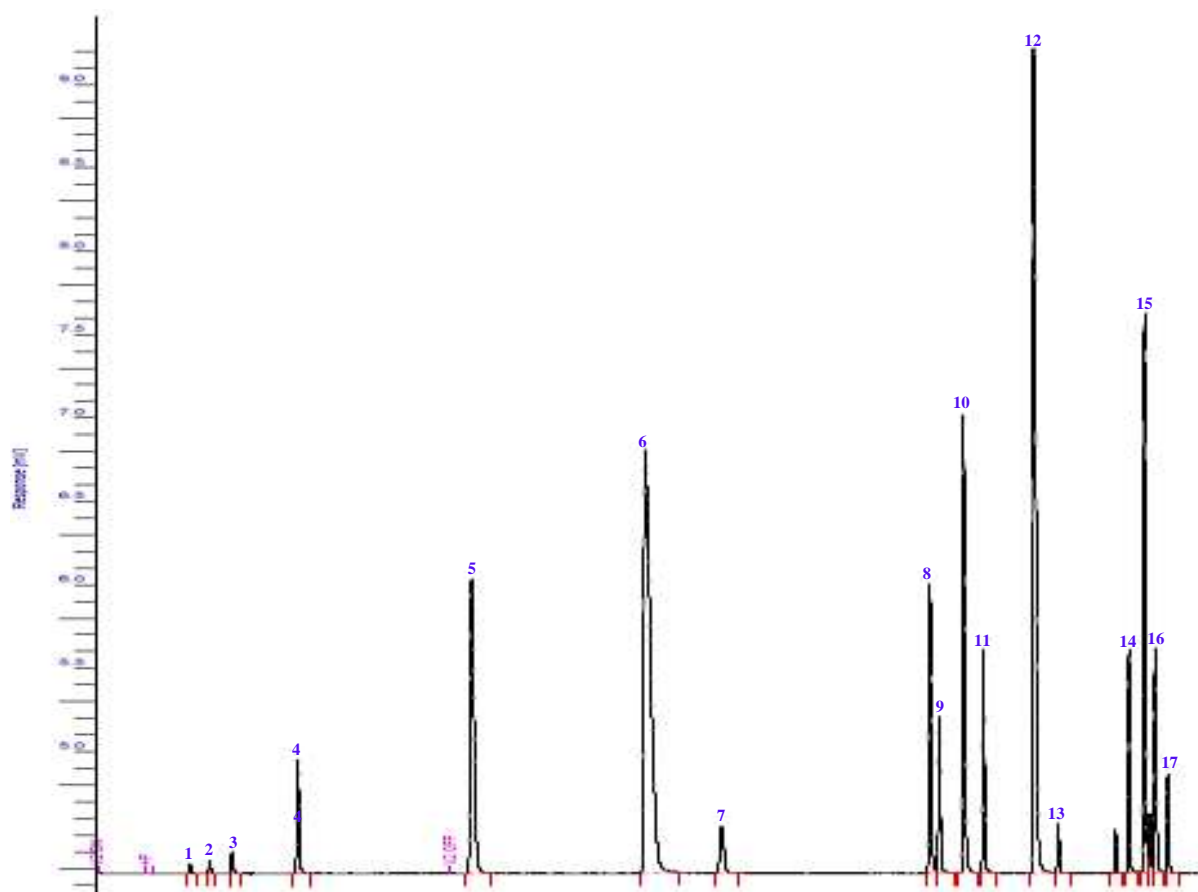
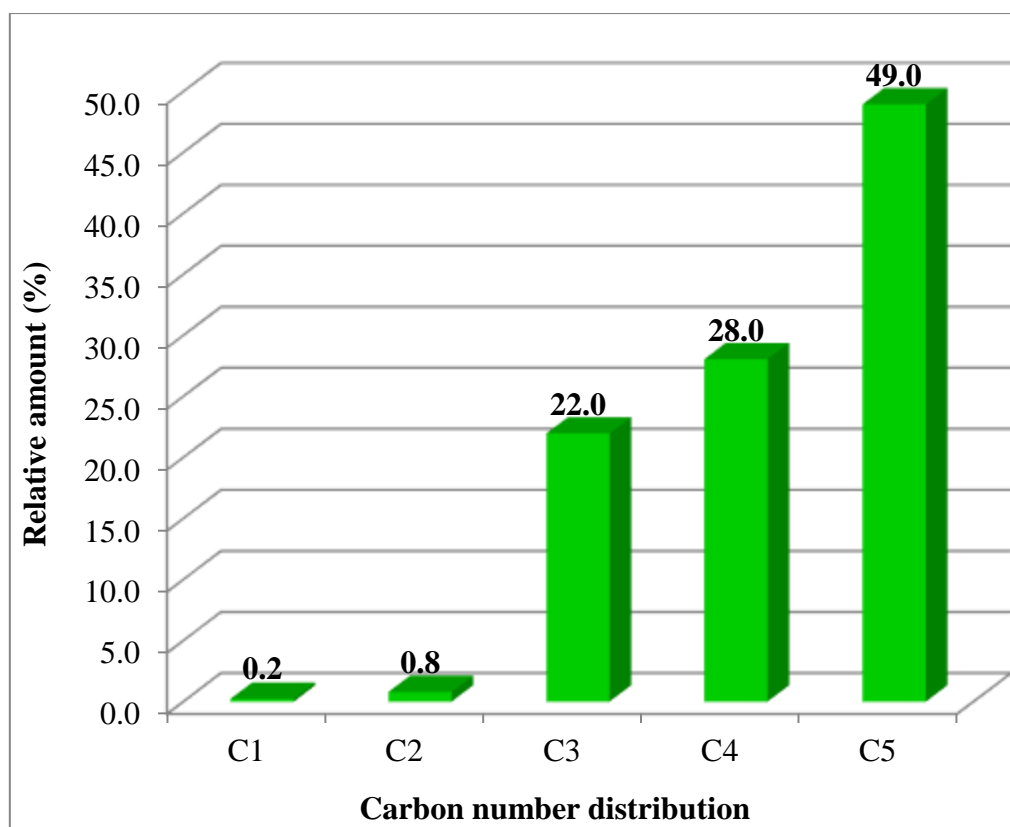


Figure 10 GC/FID Chromatogram of the gaseous product obtained at 380°C where an optimum liquid yield was obtained during thermal conversion of HDPE using sulphated zirconia catalyst.



**Figure 11** The carbon number distributions of the gaseous product obtained at 380°C where optimal liquid yield was obtained using the sulphated zirconia catalyst.

**Table 4** Summary of the hydrocarbon composition of the gaseous product obtained at the 380°C where an optimum liquid yield was obtained during thermal conversion of HDPE using sulphated zirconia catalyst.

Peak Label	Carbon No.	Hydrocarbon Compound	Relative amount (%)
1	C1	Methane	0.2
2	C2	Ethane	0.3
3	C2	Ethene	0.5
4	C3	Propane	2.9
5	C3	Propene	7.3
6	C4	Iso-butane	10.6

7	C4	n-Butane	1.2
8	C4	Trans-2-butene	7.1
9	C4	1-Butene	4
10	C4	Iso-butene	11.4
11	C4	Cis-2-butene	5.6
12	C5	Cyclopentane	20.2
13	C5	n-pentane	1.3
14	C5	Trans-2-Pentene	5.6
15	C5	3-Methyl-1-Butene	13.8
16	C5	1-Pentene	5.6
17	C5	Cis-2-Pentene	2.5

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## Conclusions

A sulphated zirconia (SZ) catalyst has been evaluated for catalytic conversion of HDPE into value added hydrocarbon products. In the presence of 10wt% SZ, the TGA onset temperature of weight loss was 187°C compared to 337°C for HDPE on its own. At 450°C only about 4wt% weight loss was achieved for HDPE whereas nearly 94wt% weight loss was achieved when mixing it with 10wt% sulphated zirconia and the temperature of maximum degradation rate ( $\Delta T_{\max}$ ) was reduced from 494°C for HDPE only to 419°C the presence of 10wt% SZ. The HDPE catalytic conversion using 10wt%SZ catalyst in a fixed-bed reactor showed an optimal liquid yield of 38.5wt% at 380°C and about 98wt% conversion. The conversion increased to 100wt% with increasing temperature to 430 °C but the liquid yield decreased to 32 wt% which was linked with high acidic property of the SZ catalyst. The liquid and gaseous products obtained at 380°C was analysed where liquid appeared to contain all the four group of

hydrocarbons in different proportion with aromatic being the dominant with 55wt%. The carbon number distribution of the liquid product was C7-C13 which is within the gasoline range composition as the amount components C13 and larger than was negligible. Gaseous composition showed different hydrocarbon compounds ranging from methane to pentane with C4 and C5 being the most dominant. The excellent activity shown by the SZ catalyst towards HDPE conversation has been attributed to its ability to initiate the HDPE cracking at low temperature of 187°C due to its high acidity surface and large external surface. This suggests that catalytic conversion of HDPE using the SZ based catalysts are particularly suitable towards liquids that have potential as fuel and chemical precursors and indicates that using the SZ catalyst for plastic waste recycling could be a cost-effective and energy-efficient method.

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Highlight

- Conversion of HDPE to liquid and gaseous hydrocarbons was conducted, where the SZ catalyst was found to have high catalytic activities at low temperature of 380°C with conversion around 100wt%, liquid yield 39.0wt%
- The performance of the SZ catalyst was associated with its excellent properties
- The results indicates the applicability SZ catalyst converting plastic waste into value-added chemicals and fuel